

## 4E01

### Metal–Ligand Cooperation in H<sub>2</sub> Production and H<sub>2</sub>O Decomposition on a Ru(II)

#### PNN Complex: the Role of Ligand Dearomatization–Aromatization

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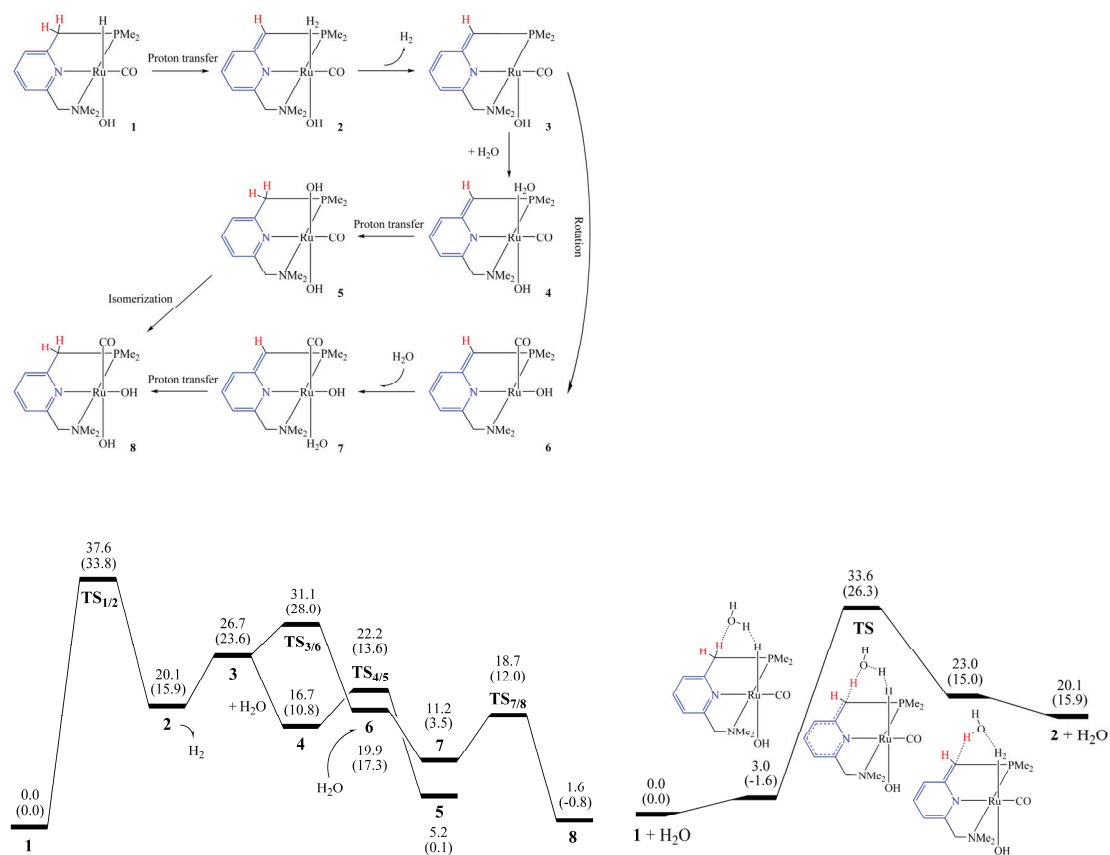
The sunlight-driven splitting of water into H<sub>2</sub> and O<sub>2</sub> is an attractive and challenging issue in science today. More recently, Milstein's group achieved a distinct scheme in which H<sub>2</sub> and O<sub>2</sub> were generated in consecutive thermal- and light-driven steps.<sup>1</sup> Heating an aromatic Ru(II) hydrido-hydroxo complex [C<sub>5</sub>NH<sub>3</sub>(CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)(CH<sub>2</sub>NEt<sub>2</sub>)Ru(H)(CO)(OH)] in refluxing water for three days resulted in the evolution of H<sub>2</sub> with formation of a *cis* dihydroxo complex. Exposure of this complex to light released O<sub>2</sub> and regenerated the starting hydrido-hydroxo complex. This scheme based on such a simple homogeneous system presents a new idea for the splitting of water. This active complex bears a tridentate PNN pincer ligand, which can donate or accept a proton via facile dearomatization/aromatization process, cooperated with the metal center. This kind of metal PNN (or PNP) complexes have been found powerful for many novel reactions than involves O–H or C–H bond activation. To our knowledge, there is little theoretical work to study this kind of metal complexes and these interesting reactions so far. Thus, in this paper, we performed detailed DFT calculations to investigate the energetics and mechanism of the thermal H<sub>2</sub> production from water splitting mediated by this Ru(II) PNN complex.

All calculations on a model system (with PMe<sub>2</sub> and NMe<sub>2</sub> groups replacing P<sup>t</sup>Bu<sub>2</sub> and NEt<sub>2</sub> groups) using the B3LYP hybrid functional were carried out with the Gaussian 03 program. The structure of each stationary point was optimized by taking into account bulk solvent (water) effects with polarizable continuum model (IEF-PCM).

The most likely pathway for H<sub>2</sub> formation and H<sub>2</sub>O decomposition on this Ru(II) PNN complex is shown in Scheme 1. In the aromatic complex **1**, a proton can transfer from the PNN ligand to the hydride and also to the hydroxyl group. But the latter is reversible. On the other hand, once H<sub>2</sub> is formed, it will be liberated but to be cleaved again. After H<sub>2</sub> liberation, the succeeding H<sub>2</sub>O decomposition occurs readily, which favorably leads to the *trans* dihydroxo complex under thermokinetics control. However, the *cis* dihydroxo complex is still the final main product, as a result of thermodynamic control. Although the overall reaction is

slightly endergonic,  $\text{H}_2$  escapes from the reaction system into gas phase at elevated temperature, driving the reaction to the product side. The rate-limiting step is the formation of  $\text{H}_2$ , which has a relatively high activation barrier of 37.6 kcal/mol (Figure 1). But water can facilitate this step as a bridging molecule (Figure 2). All of these may be the reason why the yield of the final product **8** is 45%, and 25% of **1** remains after the reaction proceeds for three days at 100°C.

*Scheme 1*



*Figure 1.* Free energy (298 K, in kcal/mol) profile for  $\text{H}_2$  production and  $\text{H}_2\text{O}$  decomposition on a Ru(II) PNN complex. The energies in gas phase are also given in the parentheses.

*Figure 2.* Free energy (298 K, in kcal/mol) profile for addition of a  $\text{H}_2\text{O}$  bridge as part of the coupling of the Ru-bound hydride with a captive proton.

## References

- [1] Kohl, S. W.; Weiner, L.; Schwartsburd, L.; Konstantinovski, L.; Shimon, L. J. W.; Ben-David, Y.; Iron, M. A.; Milstein, D. *Science* **2009**, 324, 74.